Ambient Ionization Mass Spectrometry for Chemical Imaging and Detection of Inorganic and Organic Explosives, Narcotics, and Other Forensically Relevant Analytes

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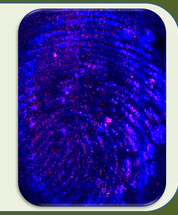


Overview

Purpose

- Develop systems for the trace detection and chemical imaging of explosive device signatures, narcotics, radionuclides, and gunshot residues under ambient conditions
- Explore platforms for desorption from solid surfaces and atomization of liquid samples for mass spectrometry (MS) analysis
- Explore direct detection and chemical mapping of trace analytes collected on swabs and spatially resolved distributions within artificial fingerprints from forensic lift tape

Methods

- Investigate the use of in-source collision induced dissociation (CID) for enhanced detection of inorganics of forensic significance
  - ✓ Explore effect of increased ion acceleration and frequency of collisions with atmospheric gas molecules for improved inorganic detection
  - ✓ Explore limits of detection for inorganic and organic compounds
- Develop ambient ionization mass spectrometry (AI-MS) platforms for forensic analysis
  - Desorption electro-flow focusing ionization (DEFFI)
  - Ultrasonic nebulization extractive electrospray ionization (USN-EESI)
  - Laser desorption/ionization (LDI)
- Develop chemical imaging systems for mapping trace analyte distributions on surfaces
- Utilize an artificial fingerprint mold and synthetic fingerprint material to investigate chemical imaging of endogenous and exogenous compounds within deposited and lifted fingerprints

Results

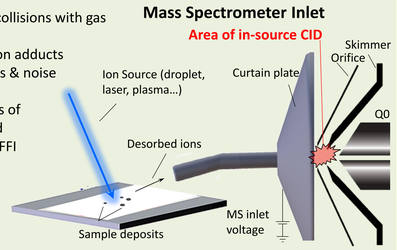
- DEFFI, USN-EESI, and LDI sources were developed and characterized for trace detection and/or mass spectrometry imaging (MSI) of forensically relevant analytes – organic/inorganic
- DEFFI demonstrated trace detection and imaging of organic/inorganic explosive compounds and explosive device signatures
- USN-EESI demonstrated the rapid detection and isotopic distribution measurements for inorganic compounds from microliter sample aliquots from complex matrices
- LDI demonstrated rapid detection and chemical imaging of inorganic compounds without sample preparation or matrix-assisted ionization

In-Source Collision Induced Dissociation

Organic & Inorganic Compounds – In-source CID

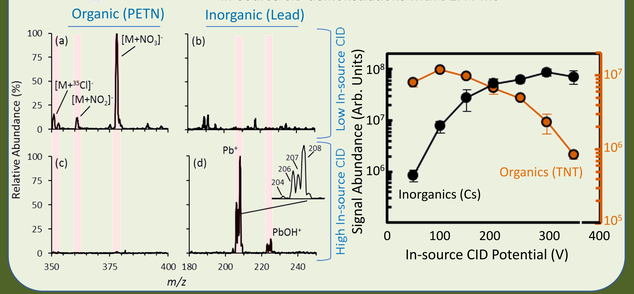
Incorporating in-source CID enhanced detection of inorganic compounds – radionuclides and inorganic explosives [1]

- ✓ Ion acceleration & increased collisions with gas
- ✓ Enhanced inorganic detection
- ✓ Fragmentation of elemental ion adducts
- ✓ Reduced organic contaminants & noise
- ✓ Isotopic measurements
- ✓ Demonstrated sub 10 ng limits of detection for both organic and inorganic compounds with DEFFI



All sources coupled to an AB Sciex 4000 Qtrap Triple-Quadrupole MS

In-Source CID demonstrations with DEFFI-MS



Desorption Electro-Flow Focusing Ionization

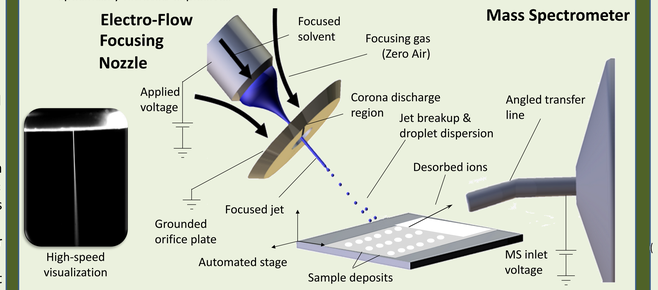
DEFFI has the potential to provide a unique multifunctional interface for the trace detection and chemical imaging of explosive device signatures, illicit narcotics, and radionuclides from surfaces with minimal to no sample preparation.

DEFFI-MS

Merging of electro-flow focusing developed by Alfonso Gañán-Calvo [2] and desorption electrospray ionization (DESI) developed by Graham Cooks [3]

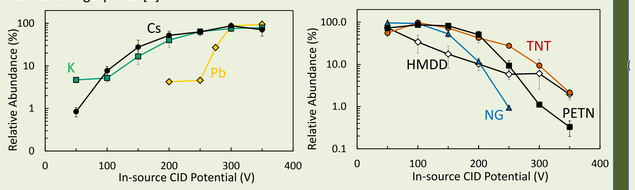
Adapted into a desorption-based ambient ionization source for mass spectrometry [1, 4-6]

- ✓ Concentric gas flow focuses solvent spray from a recessed capillary through a small orifice
- ✓ Charging electric field applied across the jet formation region – self-contained electric field
- ✓ Separates jet charging from external environment, space charge, substrate surface charging
- ✓ Enables both charged-droplet electrospray & corona discharge chemical ionization regimes
- ✓ Generates abundance of nitrate ions–enhancing adduct formation for certain compounds, specifically nitrated-explosives



Detection of Organic & Inorganic Explosive Device Signatures

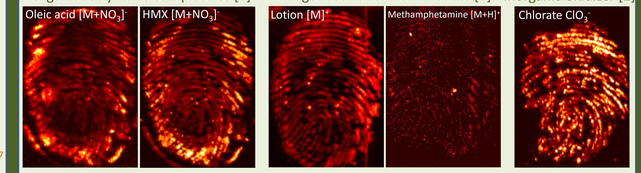
Coupling DEFFI with in-source CID for trace detection and chemical imaging from swipes and artificial fingerprints [1]



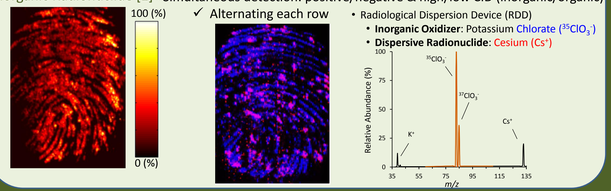
Mass Spectrometry Imaging (MSI) of Chemical Distributions

Artificial fingerprints generated from an artificial fingerprint mold and synthetic fingerprint material composed of common eccrine and sebaceous secretions at relevant levels – imaged off of forensic lift tape

Organic Fatty Acids & Explosives [6] | Endogenous Lotions & Narcotics [6] | Inorganic Oxidizer [1]



Inorganic Radionuclide [1] • Simultaneous detection: positive/negative & high/low CID (inorganic/organic)

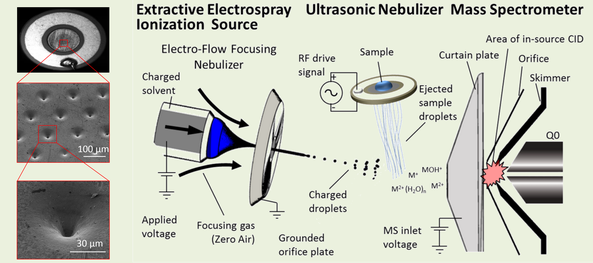


Ultrasonic Nebulization (USN)

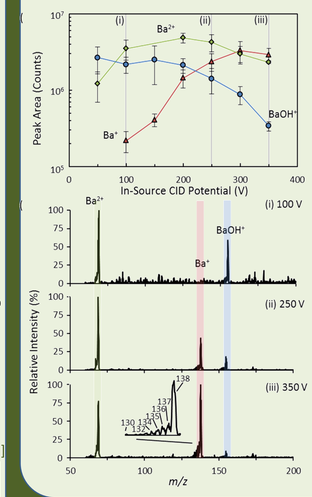
USN coupled with extractive electrospray ionization (EESI)-MS and in-source CID provides a versatile tool for the rapid detection, speciation, and isotopic identification of inorganic compounds from microliter sample solution aliquots.

USN-EESI-MS

Ultrasonic nebulization and acoustic pressure wave focusing within an array of exponential horn structures enables efficient atomization of discrete liquid samples from complex matrices



In-source CID enhanced the detection of the singly charged elemental cation species, isotopic distributions, and identified the competition between ligand loss of hydrate clusters and charge reduction from doubly charged to singly charged cations [7]

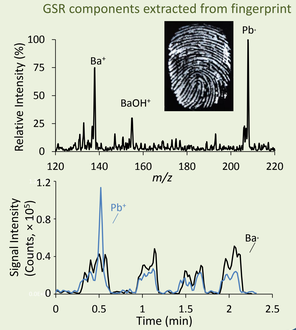


Inorganic analytes detection from complex matrices without detriment to device operation

Extractions from:

- ✓ Artificial fingerprints on automobile panel
- ✓ Artificial fingerprint material from carbon stub
- ✓ Waterway sediment (NIST SRM 1944) collected with a Nomex swab
- ✓ Shotgun slug flakes dissolved in 5 % nitric acid

GSR components extracted from fingerprint



Laser Desorption/Ionization (LDI)

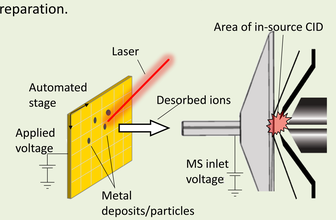
LDI can provide the detection and chemical imaging of molecular and elemental inorganic components of explosives, gunshot residues (GSR), and other forensically relevant inorganics without matrix-assisted ionization.

LDI-MS

Laser desorption/ionization enables detection and imaging of inorganic compounds and particles without the need for sample preparation.

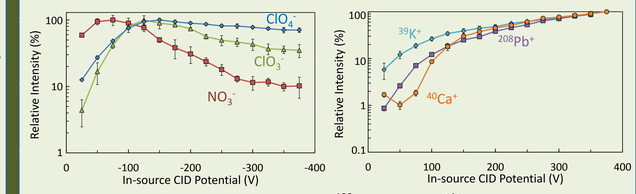
AP MALDI features	
Nd:Yag laser	
Output energy	200 uJ/pulse
Wavelength	355 nm
Frequency	Up to 200 Hz
Pulse duration	3-5 nsec
Attenuation	0-100% (by software)

MassTech, Inc.

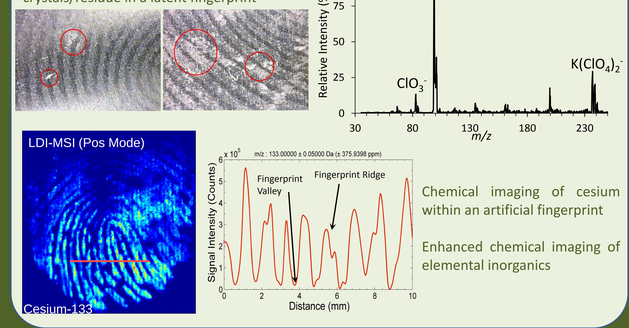


Inorganic Explosives/Oxidizers

Scanning in-source CID enabled the optimization of both the molecular anion and elemental cation from homemade explosives/oxidizers: calcium ammonium nitrate, potassium chlorate, potassium perchlorate, lead nitrate (precursor of lead azide)



Manual interrogation of potassium perchlorate crystals/residue in a latent fingerprint



Chemical imaging of cesium within an artificial fingerprint

Enhanced chemical imaging of elemental inorganics

Conclusions

- Incorporating in-source collision induced dissociation enhanced detection of both organic and inorganic forensically relevant compounds
  - ✓ Explosives, explosive device signatures, illicit narcotics, radionuclides, gunshot residue
  - ✓ Inorganic elemental and molecular speciation and isotopic measurements
- Chemical imaging of analyte spatial distributions from surfaces, swabs, carbon stubs, and within artificial fingerprints using DEFFI and LDI
  - ✓ Simultaneous imaging of positive/negative modes & high/low source CID (inorganic/organic)
- USN-EESI-MS detection and isotopic measurements of elemental inorganics from complex matrices without detriment to device operation
  - ✓ GSR components detected from extracted fingerprint (synthetic fingerprint material)
  - ✓ Detection from waterway sediment (SRM 1944) with average particle size ~ 150 µm
  - ✓ Extraction of shotgun slug flakes in 5% nitric acid and direct detection of lead component

Acknowledgements / Publications

Acknowledgements

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Relevant Publications

[1] Forbes, T.P. and Sisco, E., (2014) *Analytical Chemistry,* **86**(15), 7788-7797.
[2] Gañán-Calvo, A.M., *et al.*, (2006) *Journal of Fluid Mechanics*, **566**, 421-445.
[3] Takáts, Z., *et al.*, (2004) *Science*, **306**, 471.
[4] Forbes, T.P., Brewer, T.M., Gillen, G., (2013) *Applied Physics Letters,* **102**(21), 214102.
[5] Forbes, T.P., Brewer, T.M., Gillen, G., (2013) *Analyst*, **138**(19), 5665-5673.
[6] Forbes, T.P. and Sisco, E., (2014) *Analyst,* **139**(12), 2982-2985.
[7] Forbes, T.P., (2014) *Rapid Communications in Mass Spectrometry,* (In Press).